
जल एवं अपशिष्ट जल के नमूने लेने और
परीक्षण (भौतिक एवं रसायनिक) की पद्धतियाँ

भाग 74 वैनेडियम

**Methods of Sampling and Test
(Physical and Chemical) for
Water and Wastewater**

Part 74 Vanadium

ICS 13.060.50

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FOREWORD

‘This Indian Standard (Part 74) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality Sectional Committee had been approved by the Chemical Division Council’.

Pollution caused by substances on which biotic and abiotic agencies of decomposition are ineffective, is a unique type of pollution. Toxic trace elements and heavy metals come under the category of non-degradable pollutants. The problem caused by these elements is the fact that above a certain concentration they become harmful to living organisms.

The average abundance of vanadium in the earth’s crust is 136 ppm; in soils it ranges from 15 to 110 ppm; in streams it averages about 0.9 $\mu\text{g/l}$, and in ground waters it is generally $< 0.1 \text{ mg/l}$. The dominant form in natural waters is V^{5+} . It is associated with organic complexes and is insoluble in reducing environments. It is considered non-essential for higher plants and animals, although it may be an essential trace element for some algae and micro-organisms. Laboratory and epidemiological evidence suggest that vanadium may play a beneficial role in the prevention of heart disease. In a state where incidence of heart disease is high, vanadium was not found in water supplies. However, vanadium pentoxide dust causes gastro-intestinal and respiratory disturbances. Chronic inhalation of vanadium pentoxide dusts in industry has resulted in rhinitis, pharyngitis, bronchitis, chronic productive cough, wheezing, shortness of breath and fatigue.

Both acute and chronic poisonings have been described in workers engaged in industrial production involving use of vanadium. Most of the reported clinical symptoms reflect irritative effects of vanadium on the respiratory tract. This standard covers the gallic acid method and AAS method for determination of vanadium. There are no ISO standards currently for these methods. In preparation of this standard, assistance has been taken from Standard Methods for the Examination of Water and Wastewater (23rd Edition, 2017) published by American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF) jointly.

The composition of the committee responsible for the formulation of this standard is given at Annex A.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 ‘Rules for rounding off numerical values (revised)’.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 74 VANADIUM

1 SCOPE

This standard prescribes three methods for determination of vanadium:

- a) Gallic acid method;
- b) Direct nitrous oxide-acetylene flame atomic absorption spectrometry (AAS) method; and
- c) Induced coupled plasma spectroscopy method.

2 REFERENCES

The following standards contain provisions which through reference in this text constitute provisions of this standard. At the time of publications, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

<i>IS No.</i>	<i>Title</i>
3025 (Part 2) : 2019	Methods of sampling and test (physical and chemical) for water and wastewater: Part 2 Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)
3025 (Part 65) : 2014	Methods of sampling and test (physical and chemical) for water and wastewater: Part 65 Application of inductively coupled plasma mass spectrometry (ICP-MS) — Determination of 62 elements
7022 (Part 1) : 1973	Glossary of terms relating to water, sewage and industrial effluents: Part 1
7022 (Part 2) : 1979	Glossary of terms relating to water, sewage and industrial effluents: Part 2

3 TERMINOLOGY

For the purpose of this standard, definitions given in IS 7022 (Part 1) and IS 7022 (Part 2) shall apply.

4 APPLICATION

Depending upon the concentration range and interference levels, choice of method is made. Above methods are suitable for potable water samples. The AAS method is preferred for polluted samples.

5 SAMPLING AND PRESERVATION

The sampling bottles should be cleaned thoroughly with dilute nitric acid (6N) prior to final rinsing with distilled water. The test samples should be collected and stored preferably in polypropylene or chemically-resistant glass containers. For preservation, the samples should be acidified with concentrated nitric acid (2 ml, AR Grade) to bring down the pH to below 2. Non-acidified samples should be analyzed on the same day, while the acidified samples can be stored for a few days (up to 5 days) in a refrigerator.

6 GALLIC ACID METHOD

6.1 Principle

The concentration of vanadium present in trace amounts in water can be determined by measuring the catalytic effect it has on the rate at which gallic acid is oxidized by persulphate in acid solution. The extent of gallic acid oxidation is directly proportional to the concentration of reactants, temperature and time of the reaction. The concentration of vanadium is determined by measuring the absorbance of the sample at 415 nm and comparing it with standard solutions that undergo similar treatment.

6.2 Interference

The elements listed in the following table will interfere with the determination of vanadium if they are present in concentrations above those specified in the Table 1.

Table 1 Elements and their Concentrations above which Interference is Observed¹

(Clause 6.2)

Ion	Concentration (mg/l)
Cr ⁶⁺	1.0
Co ²⁺	1.0
Cu ²⁺	0.05
Fe ²⁺	0.3
Fe ³⁺	0.5
Mo ⁶⁺	0.1
Ni ²⁺	3.0
Ag ⁺	2.0
U ⁶⁺	3.0
Br ⁻	0.1
Cl ⁻	100.0
I ⁻	0.001

Spectroscopic determination of vanadium is a highly sensitive method, thus, only if the concentration of interfering substances are slightly above the limit of tolerance, their effect can be neutralized by dilution. Iodide ion (I⁻) or Bromide ion (Br⁻) present in traces can seriously interfere in the measurement and their effect may not always be neutralized by dilution alone. Although mercuric ion can be added to minimize the interferences by forming a complex with halides but if the mercuric ion is present in excess, it also acts as an interference. Mercuric Nitrate (Hg(NO₃)₂) present in 350 µg amount per sample can permit vanadium determination in the presence of 250 µg I⁻/l, 250 µg Br⁻/l and 100 mg Cl⁻/l. Samples containing high concentrations of I⁻, Cl⁻, and Br⁻ need to be diluted to concentrations below the values mentioned above and thereafter the specified amount of Hg (NO₃)₂ is added.

6.3 Minimum Detection Limits — Approximately 2 µg/l

6.4 Apparatus

6.4.1 Water Bath — capable of being operated at 25 ± 0.5 °C.

6.4.2 One of the following equipment is required for measurement:

- Spectrophotometer — For measurement at a wavelength of 415 nm with a light path of 1 to 5 cm.
- Filter Photometer — Equipped with violet filter with maximum transmittance near 415 nm and having a light path of 1 cm to 5 cm.

6.5 Reagents

6.5.1 Unless otherwise specified, only AR grade chemicals should be used for all the tests.

6.5.2 Vanadium-free distilled water should be used for preparing standards and reagent solution.

6.5.3 Stock Vanadium Solution — In a 1000.00 ml volumetric flask, add about 229.6 mg of ammonium metavanadate (NH₄VO₃) and dissolve in 800 ml distilled water (6.5.2). To this add 15 ml of 1 : 1 nitric acid and finally dilute the sample to 1 000 ml. (1.00 ml = 100 µg V)

6.5.4 Intermediate Vanadium Solution — Take 1.00 ml of stock solution of vanadium (6.5.3) and dilute it to 100 ml with distilled water (6.5.2). (1.00 ml = 1 µg V).

6.5.5 Standard Vanadium Solution — Take 1 ml of intermediate vanadium solution (6.5.4) and dilute it to 100 ml with distilled water (6.5.2). (1.00 ml = 0.01 µg of vanadium).

6.5.6 Ammonium Persulphate-phosphoric Acid Reagent — In 25 ml distilled water (6.5.2), dissolve 2.5 g of Ammonium persulphate (NH₄)₂S₂O₈ and bring to a boil. After the solution comes just to a boil, remove it from heat and add 25 ml concentrated phosphoric acid. Let the solution stand for 24 h before use and discard this mixture after 48 h of preparation.

6.5.7 Gallic Acid Solution — In 100 ml warm water (6.5.2), dissolve about 2 g of gallic acid (H₆C₇O₅). Heat the mixture just below boiling and filter it through Whatman No. 42 or equivalent filter paper. For each set of samples, prepare a fresh solution.

6.5.8 Mercuric Nitrate Solution — To 1000 ml of distilled water (6.5.2), add 350 mg Hg(NO₃)₂.H₂O.

6.6 Procedure

6.6.1 Preparation of Standards — Prepare the blank solutions and the standard solutions by diluting 0 to 8.0 ml of standard vanadium solution (6.5.5), i.e., 0 to 0.08 µg vanadium, to 10 ml with distilled water (6.5.2).

6.6.2 Preparation of Samples — In a suitable container, pipette out the sample (not more than 10 ml) containing less than 0.08 µg of vanadium and make up the volume to 10.0 ml by adding distilled water (6.5.2). Samples which are coloured or turbid are filtered.

6.6.3 Now add 1.0 ml of mercuric nitrate solution (6.5.8) to each blank, standard and sample, and place the containers in a water bath regulated to a temperature of (25 ± 0.5) °C. Keep the samples in water bath for 30 to 45 min, till they attain the bath temperature.

6.6.4 Colour Development and Measurement — Add 1.0 ml of temperature equilibrated ammonium persulphate-phosphoric acid reagent (6.5.6) to each container, mix properly and return to water bath. Now add 1.0 ml of temperature equilibrated gallic acid solution (6.5.7) to each container, mix properly and

keep in water bath. In order to permit the control of reaction time, add gallic acid to successive samples at 30 sec intervals or longer. After 60 min of adding gallic acid, remove the containers from water bath and measure their absorbances at 415 nm by taking water as reference. Subtract blank absorbance from the absorbance values of each sample and standard. Plot a calibration curve by taking absorbance of standards on Y-axis and corresponding concentration of vanadium (in μg) on X-axis. From the calibration curve, determine the concentration of vanadium in the unknown sample by referring to the corresponding absorbance value. Prepare calibration curve for each set of samples.

6.7 Calculation

Concentration of vanadium in sample (mg V/l) = (μg V determined by absorbance)/(original sample volume in ml).

7 DIRECT NITROUS OXIDE-ACETYLENE FLAME (AAS) METHOD

7.1 Principle

The vanadium content of the sample is determined by atomic absorption spectrophotometry. For dissolved vanadium, the filtered sample is directly aspirated to the atomizer. For total recoverable vanadium, a pre-treatment with HCl is carried out prior to aspiration of the sample. This method is applicable in the range from 5 to 100 mg/l of vanadium. However, the concentration range will vary with the sensitivity of the instrument used.

7.2 Apparatus

7.2.1 Atomic Absorption Spectrophotometer and Associated Equipment

7.2.2 Nitrous Oxide Burner Head — At roughly 20 min interval of operation, it may be necessary to dislodge the carbon crust that forms along the slit surface with a carbon rod or appropriate alternative.

7.2.3 T-junction Valve or Other Switching Valve — For rapidly changing from nitrous oxide to air, so that flame can be turned on or off with air as oxidant to prevent flashbacks.

7.2.4 Standard Volumetric Glassware

7.3 Reagents

7.3.1 Unless otherwise specified, only AR grade chemicals should be used for all the tests.

7.3.2 Vanadium-free distilled water should be used for preparing standards and reagent solution.

7.3.3 Concentrated Nitric acid (HNO_3)

7.3.4 Potassium Chloride Solution — Dissolve 250 gm of potassium chloride in distilled water (7.3.2) and dilute to 1000 ml.

7.3.5 Aluminum Nitrate Solution — Dissolve 139 gm of aluminium nitrate $[\text{Al}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}]$ in 150 ml distilled water (7.3.2). Acidify slightly with concentrated nitric acid (7.3.3) to preclude possible hydrolysis and precipitation. Warm the solution to dissolve completely. Cool and dilute to 200 ml with distilled water (7.3.2).

7.3.6 Standard Vanadium Solution — Prepare a series of standard vanadium solutions in the optimum concentration range by appropriate dilutions of stock vanadium solution (6.5.3) with distilled water (7.3.2) containing 1.5 ml of conc. nitric acid.

7.4 Procedure

7.4.1 Calibration

Prepare at least five standard vanadium solutions of 100 ml each preferably from 0.05 mg/l to 1.0 mg/l from the stock vanadium solution using appropriate dilution. Prepare a reagent blank of 100 ml volume with distilled water (7.3.2) containing 1.5 ml of concentrated nitric acid (7.3.3) and 2 ml aluminium nitrate solution (7.3.5). Aspirate the reagent blank and carry out zero adjustment. Mix 2 ml of aluminium nitrate solution (7.3.5) into the standard solutions before aspiration. Aspirate each standard solution in turn into the flame and record the absorbance readings. Most modern instruments are equipped with micro-processors and digital read-out which permit calibration in direct concentration terms.

7.4.2 Sample Preparation

Mix 2 ml of aluminium nitrate solution (7.3.5) into 100 ml of sample solution before aspiration.

7.4.3 Instrument Operation

After adjusting wavelength, install a nitrous oxide burner head (7.2.2). Turn on acetylene (without igniting flame) and adjust flow rate to the value specified by manufacturer for a nitrous oxide-acetylene flame. Turn off acetylene. With both air and nitrous oxide supplies turned on, set T-junction valve to nitrous oxide and adjust flow rate according to manufacturer's specifications. Turn switching valve to the air position and verify the flow rate in the same. Turn acetylene on and ignite to a bright yellow flame. With a rapid motion, turn switching valve to nitrous oxide. The flame should have a red cone above the burner. If it does not, adjust fuel flow to obtain the red cone. After nitrous oxide flame has been ignited, let burner come to thermal equilibrium before beginning analysis.

Aspirate a blank consisting of distilled water containing 1.5 ml concentrated nitric acid and 2 ml aluminium nitrate. Check aspiration rate and adjust if necessary to a rate between 3 and 5 ml/min. Zero the instrument. Aspirate a vanadium standard solution with a concentration near the mid-point of the optimum concentration range and adjust burner (both horizontally and vertically) in the light path to obtain maximum response. Aspirate blank again and re-zero the instrument. The instrument is ready to run standards and samples.

To extinguish flame, turn switching valve from nitrous to air and turn off acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene.

7.4.4 Sample Analysis

Rinse atomizer by aspirating distilled water (7.3.2) containing 1.5 ml conc. nitric acid per liter and zero

instrument. Aspirate a sample and determine its absorbance.

7.5 Calculation

Calculate the concentration of vanadium in microgram per litre by referring to the calibration curve prepared. Alternatively, read the concentration directly from the instrument read-out if the instrument is so equipped. If sample has been diluted, multiply by the appropriate dilution factor.

8 INDUCED COUPLED PLASMA SPECTROSCOPY METHOD

Vanadium can also be determined by induced coupled plasma optical emission spectroscopy with reference to procedure given in IS 3025 (Part 2). Likewise, induced coupled plasma mass spectroscopy with reference to procedure given in IS 3025 (Part 65) can also be used for the determination of vanadium.

ANNEX A

(Foreword)

COMMITTEE COMPOSITION

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